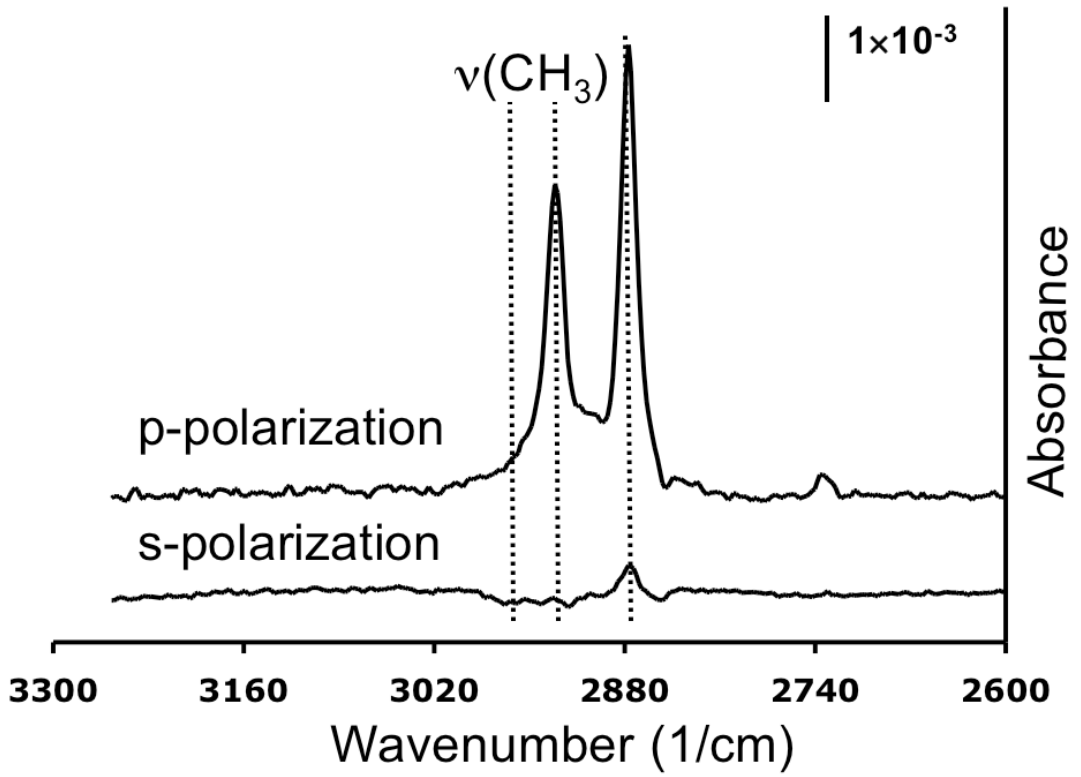

Figure S1 Spectra obtained when referencing a $C_2H_3D_2$-Si(111) sample to a $C_2H_2D_3$-Si(111) sample. The shoulder and the two prominent peaks, at 2960 cm^{-1}, 2931 cm^{-1}, and 2877 cm^{-1}, in the p-polarized spectrum must originate from the CH_3 group thus further supporting the assignment of those peaks.

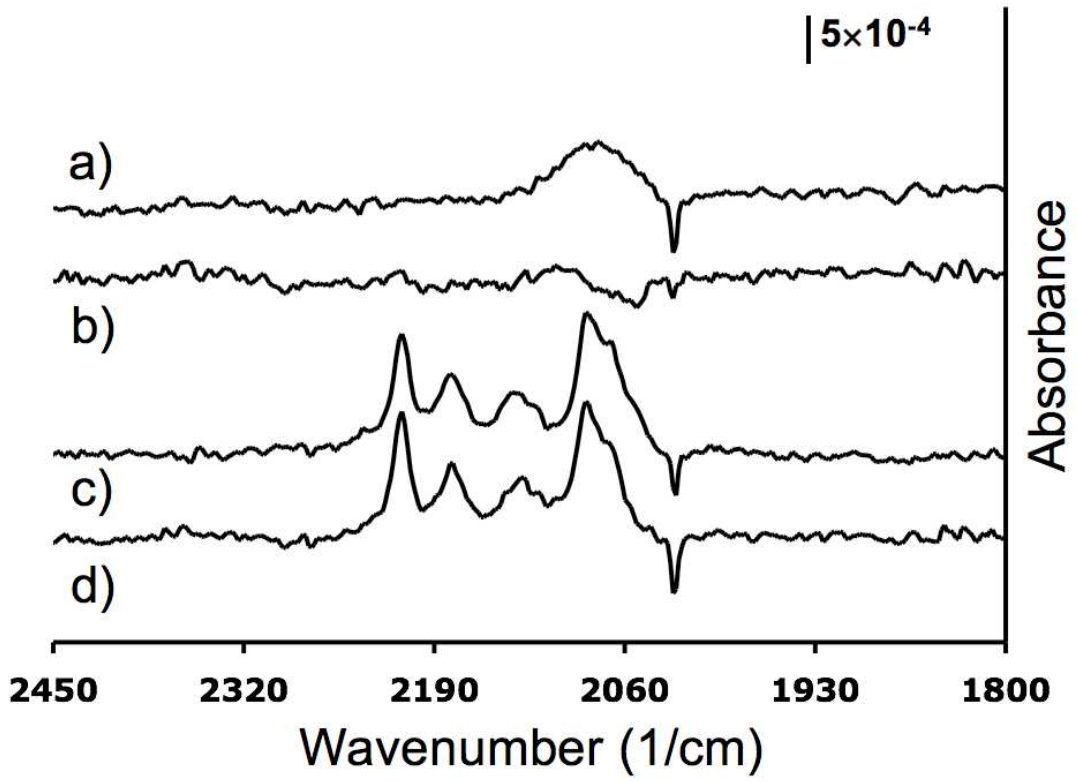

Figure S2 Spectrum a shows the p-polarized Si-H peak of a C_2H_5-Si(111) surface; spectrum b being the subtraction result of spectrum c and d; spectrum c showing the p-polarized C-D stretch region for a C_2D_5-Si(111) surface synthesized using all deuterated solvents; and spectrum d showing the p-polarized C-D stretch region for a C_2D_5-Si(111) surface synthesized using all protic solvents. Note that no residual signal attributable to the Si-H stretch is detectable in spectrum b.

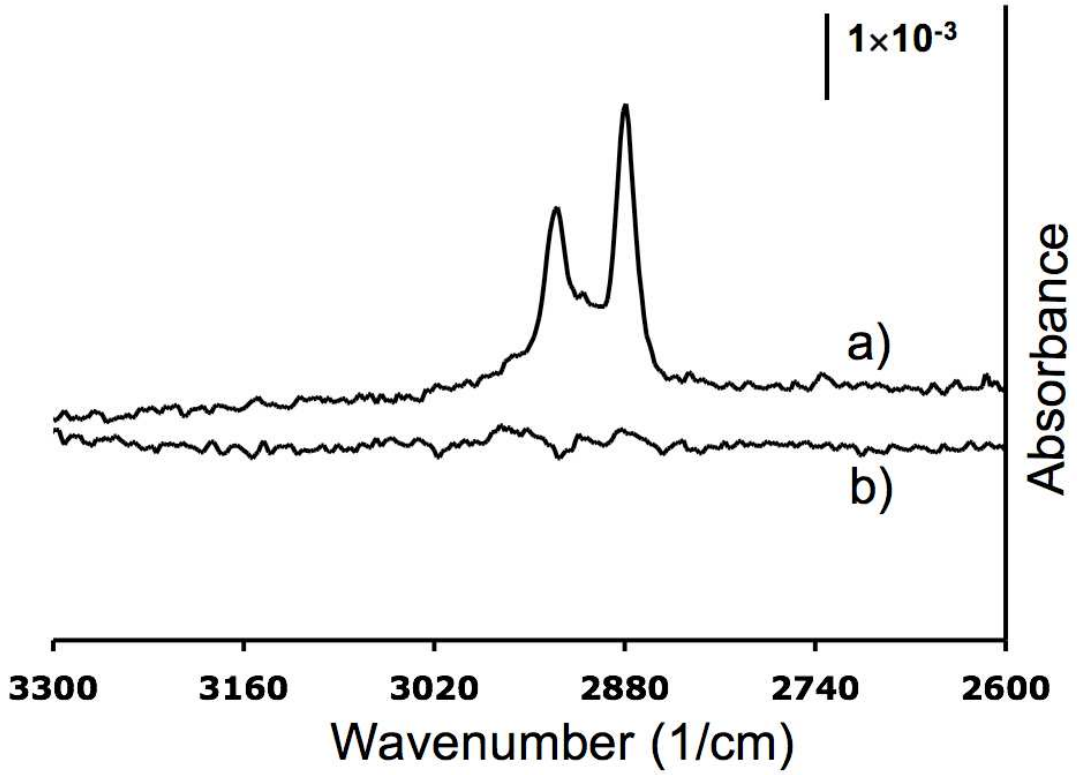

Figure S3 The bottom spectrum (b) shows the subtraction result of a p-polarized spectrum from a C_2D_5-Si(111) surface synthesized using all protic solvents, and a p-polarized spectrum from a C_2D_5-Si(111) surface synthesized using all deuterated solvents. The top spectrum (a) is the p-polarized spectrum of a C_2H_5-Si(111) surface included as a scale reference. Note that no signal attributable to C-H stretching is present in the bottom spectrum suggesting that no side reactions involving the solvents took place, to the limit of detection.